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Structure and photophysical processes in 0D&1D InGaN composite materials

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Anotation

The thesis describes structural and photophysical properties of MOCVD grown GaN nanowires (NWs) and InGaN quantum dots (QDs). For both cases it is shown that *ex-situ* RHEED measurements are feasible and yield qualitative information about the structure. In combination with other methods, firstly, it is shown that non-metallic catalyst assisted GaN NW characteristics differs from traditionally obtained ones, where catalyst seems to be located at the base of nanowire not top, and growth direction slightly differs from c-axes when synthesized on GaN (0001) surface, which results in semipolar NW structures. Secondly, for InGaN composite it was possible to recognize a strongly strained lattice in case of high indium concentration within QDs.

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Abbrevations

AFM	Atomic force microscopy
EDX	Energy-dispersive X-ray spectroscopy
IR	Infradred light
L_0, L_1, L_n	Laue zones
LED	Light Emiting Diod
MBE	Molecular beam epitaxy
MO	Metalorganic
MOCVD	Metalorganic chemical vapour deposition
MOVPE	Metalorganic vapour phase epitaxy
nano-LED	Nano scaled LED
$\operatorname{nano-SIMS}$	High resolution Seconday Ion Mass Spectrometer
NW	Nanowires
PL	Photoluminescence
QDs	Quantumdots
RF	Radio frequency
RHEED	Reflection high-energy electron diffraction
SEM	Scanning electron microscope
SK	Stranski–Krastanov growth
TEGa	Trietilgallium
TEM	Transmission electron microscopy
TMGa	Trimetilgallium
TMIn	Trimetilindium
VLS	Vapor-liquid-solid
VSS	Vapor-solid-solid
XRD	X-ray Diffraction
ZOLZ	Zero order Laue Zone (L_0)

Introduction

The demand for ever smaller devices and increased efficiency makes scientists look for a ways to reduce the size of the existing semiconductor elements. So far, the methods used in lithography have been able to justify the market demands, but the technology cannot be applied to nano scale light emitting diode production. The solution lies in the epitaxial grown structures. By vapor-liquid-solid (VLS) growth mechanism, it is possible to obtain nanocrystals with a large length to diameter ratio, which is typically referred to as nanowires (NWs). Light-emitting diodes (LED) structures formed on such a nanowire (nano-LED) are superior to conventional thin films diode. It is expected that the semiconductor elements that are built on defect-free nanowires, will provide high quantum efficiency outcome for useful energy transfer. NW serves as an ideal electron transport tunnel, which effectively transfer energy to the LEDs active layer containing quantum dot (QD) structures. The concept of "QDs on NWs" embodies many positive characteristics:

- 1. high mobility of charged particle transport;
- 2. large active area (nanowire wall);
- 3. small Auger electron scattering (no efficiency decline with increase in power);
- 4. efficient light extraction (nanowires as optical fiber);
- 5. possible to use cheap substrates;
- 6. 30% fewer steps for LED component industry.

Recently, attention is paid to the group III nitrides for semiconductor element development. By using such an elements as AlN, GaN, and InN the band gap of semiconducting material can be chosen from the wide energy range of 6.2 - 0.7 eV. Already the emission energy for LEDs based on only $\ln_x \operatorname{Ga}_{1-x} N$ compound can be produced for the entire visible spectrum. Also the InN and GaN band gap offset stimulates the hole and electron tunneling probability from GaN nanowires to InGaN quantum well structures [1]. Typically $\ln_x \operatorname{Ga}_{1-x} N$ was used only for UV LEDs where indium concentration did not exceed 20%. For higher concentration indium segregation occurs where metallic indium clusters are formed within the active layer. This limit can be overcome by forming a nonscaled 0D structures or also called quantum dots. Such a high indium concentration containing QD synthesis occurs by epitaxial Stranski-Kastranow (SK) growth method [2]. It is already shown that such an LED, containing InGaN QD active layer, can be produced for whole visible light range [3–6]. If the layers are grouped one above the other to form a multi quantum well structure, it is possible to generate white light emitting components without the need of a final phosphorescent layer. These structures can be formed on the basis of nanowires obtaining high efficiency and capacity nano-LEDs.

Aim of the work

This work aims to separately study indium and gallium nitride based nano-LED structural elements, in order to be able in the future to develop nanoscale light emitting diodes.

To synthesis free standing GaN nanowires the structure of non-metallic catalyst grown nanowires has to be investigated. In order to derive the growth characteristics, both SEM and TEM methods are used in combination with RHEED measurements.

Secondly, a method to synthesize high indium concentration InGaN QDs by MOCVD has to be developed, where the resulting composite morphology is investigated by AFM and SEM, optical properties are derived from time resolved PL and structure is determined by RHEED measurements. In order to get In/Ga concentration relation on the surface the nano-SIMS measurements are carried out.

Authors contribution

Publication I: "Ex situ investigations of MOCVD-grown gallium nitride nanowires using reflection high energy electron diffraction." A. Voitkans, L. Dimitrocenko, P. Kulis, S. Bartling, I. Barke, K-H. Meiwes-Broer and I. Tale, *IOP Conf. Ser.: Mater. Sci. Eng.*, 23(1):012038, 2011 [7].

The author has performed an ex situ RHEED investigations on MOCVD grown GaN nanowires, analyzed data and written the body of an article.

Publication II: "Dynamics of exciton creation and decay processes in composition – disordered InGaN thin films.", L. Dimitrocenko, P. Kulis, A. Sarakovskis, I. Tale, and A. Voitkans, *IOP Conf. Ser.: Mater. Sci. Eng.*, 23(1):012001, 2011 [8].

The author has developed tools for data analysis and helped with data processing procedures.

Publication III: "Localization dynamics of exciton luminescence in $In_x Ga_{1-x}N$ epitaxial films." I. Tale, L. Dimitrocenko, P. Kulis, G. Marcins, A. Sarakovskis, and A. Voitkans, *IOP Conf. Ser.: Mater. Sci. Eng.*, 15:012059, 2010 [9].

The author provided a data analysis tools for acquired luminescence spectras as well as did part of data analysis.

Publication IV: "Growth temperature influence on the GaN nanowires grown by MOVPE technique." L. Dimitrocenko, K. Kundzins, A. Mishnev, I. Tale, A. Voitkans, and P. Kulis, *IOP Conf. Ser.: Mater. Sci. Eng.*, 23:012026, 2011 [10].

The Author has prepared a catalyst layer for GaN nanowire growth and participated in discussions, and editing of paper. **Publication V:** "Size-dependent alignment of iron nanoparticles upon deposition onto W(110)." A. Kleibert, A. Voitkans, and K.-H. Meiwes-Broer, *Physical Review B*, 7:073412–073415, 2010 [11].

The author has assembled the experimental RHEED and participated in all experiments as described in the article. Also has made a full data analysis and wrote algorithms for electron diffraction pattern simulations.

Publication VI: "Reflection high energy electron diffraction as a tool in cluster deposition experiments." A. Kleibert, A. Voitkans, and K.-H. Meiwes-Broer, Physica Satus Solidi (B), 247:1048–1055, 2010 [12].

The author has assembled the experimental RHEED and participated in all experiments as described in the article. Also has made a full data analysis and wrote algorithms for electron diffraction pattern simulations.

Scientific novelty

It is shown that RHEED is appropriate method for out of chamber synthesize GaN nanowire and $In_xGa_{1-x}N$ QD investigations, giving a quality information on structure in relation to the substrate surface.

With LiF catalyst MOCVD-grown GaN nanowires on GaN (0001) surface exhibit semipolar structure PL characteristics. What is also confirmed by RHEED and TEM measurements, showing a potential $[2\overline{1}\overline{1}0]$ growth direction, in contrast to typically expected results from a metallic catalyst VLS grown GaN structures.

Under definite size limit of about 30 nm in height the indium concentration can be increased above 20% within $In_x Ga_{1-x}N$ QDs. From RHEED measurements it was derived that in the case of high indium flux and longer growth times within MOCVD reactor after initial QD synthesis a clean InN is formed on top initial particles. If the growth time is reduced and QDs up to 15 nm in height are formed, it is possible to recognize a highly strained crystallographic structure, that could be an explanation for the observed PL band broadening for $In_x Ga_{1-x}N$ with relation to increase of x stoichiometric ratio.

1 Theoretical background

1.1. Gallium nitride structures

Group-III nitrides form thermally and mechanically stable wurtzite crystallographic structure due to a small nitrogen atom when compared to III group elements. This holds true for high temperature thin films grown on sapphire (0001) wafers, but at low temperatures some zincblende structure insertions can be observed [13]. It is possible to hinder the wurtzite structure formation by choosing GaAs(001), Si(001) or Mg wafers [14, 15]. As typical production of group-III nitride occurs along c axis, thin films face two possible polarizations, where the top layer consists of either nitrogen or a III-Group atom (Fig. 1.1.). The yield can be controlled with a low temperature nucleation layer thickness, as typical N-polar GaN thin film has a rough surface and is not suitable for the development of semiconductor elements.

As a substrate for GaN synthesis most commonly used material is sapphire (0001). It has an advantage of similar crystallographic structure when compared to a cheaper alternative – silicon. Still a thin film of low temperature nucleation layer is required to compensate the crystallographic constant mismatch of 13%. The complete information on substrates for GaN synthesis is available elsewhere, at ref. [16].

1.1.1. MOCVD synthesis

The metal-organic chemical vapor deposition (MOCVD) is a chemical vapor deposition method used to produce single or polycrystalline thin films. In contrast to the molecular beam epitaxy (MBE), the crystalline films are obtained as a result of chemical reactions, rather than by thermal deposition method. The process takes place in the presence of various gases at low pressures. This method is suitable for thermally



1.1. Figure. GaN wurtzite structures (a) c surface symmetry and (b) planar view showing polar structure.



1.2. Figure. MOCVD thin film synthesis process (a), the interference pattern as mesured by the laser system (b).



1.3. Figure. VLS nanowire growth mechanism by the use of eutectic droplets.

metastable compounds and has become one of the main tools for the manufacture of semiconductor elements.

For this thesis an AIXTRON MOCVD equipment is used. It is designed not only for 0D, 1D and 2D nitride materials synthesis, but also other material acquisition (eg, Graphene, silicon nanowires, etc.). Material deposition is done within a cold wall quartz reactor. 2" wavers are placed on a block of graphite, which is heated with assistance from RF induction generator. This way it is ensures that the reaction between the gases takes place only when the hot surface of the substrate is reached (Fig. 1.2.(a)).

To obtain the information about the dynamics of the process, the reflected laser light intensity is monitored by PC in real time. From interference patter it is possible to identify the start of nucleation layer growth and asses the thickness of grown buffer layer (Fig. 1.2.(b)).

Previous studies indicated that this equipment can be used to obtain high-quality UV LED [17], and is suitable for GaN nanowire synthesis [10].

1.1.2. GaN nanowires

Ideally, the nano-LED structure is built on top of the homogeneously ordered nanowire array. Typical NW synthesis is done by vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) mechanism. At the start, the sample surface is coated with a catalyst thin film (Fig. 1.3.(1)). Than sample is placed within the reactor and, at that temper-atures above the melting, catalysts forms droplets (Fig. 1.3.(2)). Reagents are rapidly absorbed by the surface and dissolves within the catalyst until an eutectic point is reached (Fig. 1.3.(3)). Further concentration of the solution can rise no more and any excess material is transferred to the contact surface. This results in a fast crystal growth under eutectic point, forming nanowire structures (Fig. 1.3.(4)). The product diameter is dependent on the initial particle size, where minimum is determined only by the limit of the thermodynamic properties of the fluid.

On our equipment we have tried to obtain GaN NWs using metallic catalysts like gold. But it was found that process is unstable and with poor repeatability. That can be explained by the low solubility of nitrogen within gold [18]. Similar findings are described by other groups, that report no NW growth with a use of Au catalyst [19, 20]. The drawback can be avoided by choosing catalyst from the list of GaN solvents. Already some compounds as LiF and Li₃N are used in producing GaN crystals at low temperatures - around 760 °C [21]. In the result, by using LiF as a catalyst, the GaN nanowire VLS growth became stable and first results were reported soon after [10]. Further in this work non-metallic catalyst grown GaN NWs are investigated and discussed in more details.

1.1.3. InGaN quantum dots

If $\ln_x \operatorname{Ga}_{1-x} N$ with x > 0.05 is deposited on GaN buffer layer, by a Stranski– Krastanov growth method a quantum dot structure is formed. After a homogeneous wetting layer formation with 1 - 2 nm thickness, to reduce the surface energy, InGaN forms islands that are localized on the surface dislocation [22–24]. Indium concentration within QDs can be controlled by the amount of raw material in the reactor and the temperature of the selected process. At temperatures above 700 °C indium is not fully incorporated within the crystalline structure, but at reduced temperatures, the concentration of In becomes saturated and approaches the ratio of TMGa and TMIn molar ratio [24, 25].

The InGaN QD system serves as an excellent trap, where charged particles are localized and their migration to non-radiation recombination is hindered. Thus, it is expected to have a high efficiency luminescence yield when QD concentrations is close to dislocation number on buffer layer surface [22]. Usually a single layer of QDs is not sufficient to observe the effect, one must account for multilayer structures, where the density per unit volume is increased by the order of magnitude [26].



1.4. Figure. nano-LED concept with upright n-GaN nanowires and the top multilayer QD structures (a), by changing the indium concentration within $In_x Ga_{1-x}N$ multi QD layer, the emission maximum can be tuned throughout the visible spectrum region (b).

1.1.4. Nano-LED structures

In a standard white semiconductor LED, phosphors are excited by ultraviolet (UV) emission to produce a white light, but the spectral Stokes loss, in the conversion between UV and visible light, limits the final efficiency. Thus, if a single nanocolumn LED chip can emit the whole visible range with a proper emission profile, the white LED can be released from the Stokes loss limitation for the quantum efficiency.

It is shown, that single emission wavelength nano-LEDs gives a promising results. Such LED have been obtained at Sophias University (Tokyo) year 2007, under the guidance of Professor Katsumi Kishino [3]. At the time good quality NWs could be obtained only by MBE method, but that gave the possibility to test the concept on real applied devices. Because of the simplicity of MBE method a n-Si(111) substrate could be used, where the diode structure was built on top of free standing nanopillars (Fig. 1.4.(a)). Now by changing the InGaN QDs indium concentration it was possible to cover the whole range of visible light emission from 436 nm (blue) to 614 nm (red) as seen in Fig. 1.4.(b).

Although, a nano-LED concept is well known and proven to be effective, still the challenge remains to develop the method for GaN synthesis on industrial devices such as MOCVD.

1.2. Methods for nanostructure analysis

1.2.1. Optical spectroscopy

The experimental apparatus consists of a laser (Ekspla NL202), monochromator (SR-303i), iStar ICCD camera and computer for data recording (Fig. 1.5.). Laser pulse operating frequency is 10 Hz with selectable emission wavelength within 266 – 350 nm range. With the help of mirrors and lenses the light is focused on the surface of the sample. The resulting fotoluminescence (PL) is acquired by the ICCD camera and register on the computer. Using a built-in time delay generator it is possible to resolve PL evolution in time. The kinetic measurement is started by the signal sent from the laser power source module. After set delay time camera takes a PL spectrum with a minimum exposure window of 6 ns.



1.5. Figure. Experimental setop for PL spectra detection

1.2.2. RHEED structural analysis

Reflection high-energy electron diffraction (RHEED) is a technique used to characterize the surface of crystalline materials. RHEED systems gather information only from the surface layer of the sample, which distinguishes RHEED from other materials characterization methods that also rely on diffraction of high-energy electrons. Although this method has been known since the last century, it has gained recognition in modern times and is widely used for *in-situ* measurements for thin films growth control. In this work, it was shown that RHEED can be used also for out of the chamber grown crystalline nanostructure investigations [7].

The RHEED system used for GaN NW and InGaN QD analysis were constructed by the author during master's studies at the University of Rostock and is described in detail within the master's thesis [27]. In general, the device consists of an electron gun, a vacuum chamber with sample holder and a fluorescent screen. Now differential pumping system provides the electron gun operation, starting with 1×10^{-11} mbar up to 1×10^{-5} mbar bar pressure. The electron energy can be selected in the range of 10 - 30 keV. Improved sample holder allows the specimen to be heated up to 500 °C.

For data analysis a simple understanding of kinematic scattering is necessary. In the case of a surface diffraction inverse lattice of topmost atoms extends to infinite rods. Thus, every atom finds the intersection with Ewald's sphere fulfilling so called 2D Laue diffraction condition [27, 28]. In case of nanostructured surface, similar to the TEM device, in RHEEED experiments electron energy is large enough to pass through few tens of nanometers of material. In this not all reflexes are allowed and Laue equation has to fulfill 3D inverse lattice conditions.

Now if both 2D and 3D diffraction is visible on the RHEED screen, it is easy to recognize one from another. If the sample is rotated with respect to the incident electron beam 2D diffraction pattern is continuously changing while 3D diffraction spots discretely disappear and appear as predicted by Laue equation. In the special case, when surface contains randomly oriented crystalline structure, all possible reflections are shown simultaneously, what gives the rise to circular diffraction rings also called Debye-Scherrer rings [29].



1.6. Figure. NanoSIMS prinipal schematics.

This gives the advantage for a RHEED device to investigate nanowire and quantum dot structure with respect to surface alignment, as shown in similar experiments for deposited iron cluster on tungsten surface caried by the author [11, 12].

1.2.3. nano-SIMS analysis

The Cameca NanoSIMS 50 is an ultra-high resolution chemical imaging instrument combining the sensitivity of dynamic SIMS with a lateral resolution below 100 nm. The NanoSIMS represents the state-of-the-art *in situ* microanalysis by secondary ion mass spectrometry, combining unprecedented spatial resolution with ultra-high sensitivity (<200 atom detection limit). The nano-SIMS couples a high transmission, high mass resolution mass spectrometer with an array of detectors, enabling simultaneous collection of 8 elements or isotopes originating from the same sputtered volume of a sample (Fig. 1.6.). The primary ion beam ($^{133}Cs^+$ or $^{16}O^-$) can be scanned across the sample to produce quantitative secondary ion images. This capability for multiple isotope imaging with high precision and accuracy with nanometer scale spatial resolution is unique to the nano-SIMS and provides a novel new approach to the study of the isotope and trace element distributions.

2 Results and discussion

2.1. Synthesis of GaN buffer

For MOCVD synthesis of the high-quality GaN buffer layer a 2-inch sapphire (0001) substrate is used. Gallium is acquired from pure trimethylgallium (TMGa) or triethyl-gallium (TEGa) metalorganic (MO) compounds. The nitrogen source is ammonia (NH_3) gas. The purity of all raw materials is better than 2 ppb. During the process GaN is formed by reaction between group III and V elements:

$$Ga(CH_3)_3 + NH_3 \rightarrow GaN + 3CH_4$$

GaN buffer layer growth procedure is shown in the Figure 2.1.. The reagent transport to the reactor is done by the carrier gas - hydrogen. During the whole process the pressure is kept at 100 mbar. Procedure starts with Al_2O_3 desorption at 1200 °C for 10 minutes, followed by surface nitridation and 7 minutes long growth of low temperature nucleation layer at 500 °C temperature. At a time when the reactor temperature is raised to 1170 °C amorphous nucleation thin film recrystallizes to form a good basis for monocrystalline GaN buffer layer. Typical 30 min growth time produces 1.5 µm thick layer.

The quality of the GaN buffer layer is controlled by sequential AFM measurements. In the case of low quality sapphire wafers, the resulting surface is covered with low density nanocrystalline structures that may interfere with further experiment development (Fig. 2.2.(a)). In order to reduce this influence, it has been found that a repeated low temperature layer on top of the first effectively reduce the dislocation impact on final high temperature GaN buffer. The process requires only a thin (>0.5 µm) GaN buffer to



2.1. Figure. A typical MOCVD process of GaN buffer layer preparation.



2.2. Figure. AFM measurements (a) GaN buffer layer of one and (b) two nucleation layers



2.3. Figure. SEM images of GaN nanowires with (a) 4350× and (b) 20000× magnifications

be grown, as described in the previous paragraph. In this case, a second buffer results with a high quality GaN surface with roughness below few nanometers and number of dislocations in the range of $(1 - 10) \times 10^9 \text{ cm}^{-2}$ (Fig. 2.2.(b)). A similar procedure is applied to reduce the number of dislocations and to form a crack free GaN buffer on Si substrates [30, 31].

2.2. Synthesis of GaN nanowires

After the GaN buffer layer preparation the sample is delivered to the thermal deposition system, where a pure LiF crystal is used as a catalyst source. With help of a quartz resonator the thin film thickness can be set with 0.5 Å precision. Afterwards sample is returned to the MOCVD equipment. GaN nanowire synthesis takes place in H₂ atmosphere, 300 mbar pressure and with V/III group element ratio of 50. It has been observed that the nanowire growth occurs within the temperature range from 740 to 890 °C, where the best results are obtained at 800 °C. That is believed to be close to the eutectic solution formation temperature (in comparison pure LiF has a melting point



2.4. Figure. SEM image at $20k \times$ of ordered GaN nanowires shows a typical 60° growth direction with respect to each other, also highlighted by red triangle. Inset (a) show area on sample show cluster of NWs, (b) a single nanowire tip at $162k \times$ magnification.

845 °C) [10]. NW growth rate is an indication for VLS growth mechanism. It is in the range of $1 - 2 \,\mu\text{m/min}$, which is much higher when compared to GaN epitaxy.

It has been shown that the nanowire morphology (density, diameter and shape) can be adjusted not only by selecting the process temperature, but also by changing the thickness of the catalyst. One of the first results were obtained using a relatively thick catalyst layer (above the 100 nm). In the result a thick and high density of thin nanowires has been obtained. The SEM images in Fig. 2.3. show the sample at $4350 \times$ and $20000 \times$ magnifications. The candle like shape of larger NWs is attributed to simultaneous epitaxial growth. Presence of small nanowires accounts to a secondary growth process within the reactor. The sample comprises of non-uniform distributions of nanowires, including areas with almost clean GaN surface. Further investigation of the sample has been done using the RHEED apparatus similarly as has been described in ref. [11, 12].

By choosing a thinner catalyst layer with a thickness of 50 nm it is possible to get a uniform GaN nanowire structures. In the Figure 2.4. it is shown the picture of nanowires with a diameter up to 300 nm. At a high density, they form a triangular shapes (for a better overview it is highlighted by a red triangle in Fig. 2.4.(a)). The most important feature to note here is a pointed tip for NWs, that has no presence of catalyst as seen in Fig. 2.4.(c). This is a first indication that VLS growth occurs at the base of nanowire where catalyst does not lose the contact with a surface.

In order to verify the previous conclusions, acquired NWs were investigated by transition electron microscope (TEM). For this, GaN structures from surface were transferred onto copper grids and into TEM. Because studied nanowires has a large diameters, in order to ensure the best contrast, the electron energy of 200 keV were selected, which ensures electron transition through almost a 100 nm thick NW as it is shown in Figure 2.5.(a).



2.5. Figure. Two nanowire TEM images: (a) in diameter - 100 nm, on the left the electron diffraction pattern and EDX spectrum, (b) diameter - 150 nm with distinguishable triangular shape, also highlighted by a red frame.

In case of diffraction pattern direct electron beam was left open and the film was overexposed, but, by image processing, it was possible to remove most of the background. The recovered powder diffraction pattern is characterized by wurtzite GaN crystallographic lattice with a low angle inwards with respect to the nanowire growth direction vector (as indicated in the inset of the Figure 2.5.(a) by white arrow marker [0001]). The EDX spectrum confirms Ga presence on the sample. Nitrogen is not detected due to equipment's poor sensibility for this element. Similar to the SEM images, the nanowire in Figure 2.5.(b) has a triangular shape with no trace of catalyst material at the tip.

2.3. Nanowire structural investigation with RHEED

The primitive GaN unit cell contains 4 atoms, in the case of the wurtzite structure (space group P63mc), where GaN (0001) forms a surface atom arrangement of hexagonal symmetry. In RHEED experiments only the surface layer contributes to the diffraction pattern, fulfilling Laue diffraction conditions of the 2D lattice. Resulting diffraction images of the GaN (0001) surface along the [110] direction (Fig. 2.6.(a)) and rotated by 30° (Fig. 2.6.(b)) confirm hexagonal symmetry of the surface layer with a crystallographic constant a = 3.2 Å. Rotation angles with respect to the incident electron beam are given relative to the lattice direction [110]. The long streak structure close to the horizon level (at the zero order Laue zone) and elongated diffraction dots at the first order Laue zone (FOLZ) are an indication of surface roughness. It amounts 20 Å on average as measured by atomic force microscopy (AFM). For all images, a diffuse electron background, as a result of sample contamination due to transport through the air, has been suppressed by Laplacian differentiation and subsequent Gaussian convolution [32]. Nanowire contribution to the diffraction pattern is seen in Fig. 2.6.(c,d), where



2.6. Figure. RHEED image of a pristine GaN (0001) surface (a,b) and together with NWs (c,d) at two directions [110] (a,c) and [100] parallel to incident electron beam. Top most insets show the respective real lattice, while the bottom illustrations sketch preferred NW orientation on the surface. The electron incident direction (denoted by thick arrows) with respect to the NW wurtzite lattice corresponds to $[1\bar{1}00]$ in (c) and $[2\bar{1}\bar{1}0]$ in (d), respectively.

an area with a higher concentration of nanostructures has been chosen on the sample. Due to electron transmission through the NWs diffraction Bragg spots are formed as defined by Laue conditions for a 3D lattice. In the RHEED experiment, the electron beam size projected onto the surface is approximately 1-5 mm². Thus, each diffraction pattern shows a sum of all nanowire contributions within this area. As a result, sharp dots at high symmetry directions can occur because of the nanowires' preferred epitaxial orientation with respect to the surface layer (as illustrated on the right side of Figures 2.6.(c,d)), where an orientation of c direction of GaN wurtzite lattice has been observed. Similar findings have been confirmed for MBE and plasma assisted MBE grown GaN NWs showing the same type of RHEED patterns for oriented nanowires [33, 34].

Diffraction from randomly oriented crystalline structures (Fig. 2.3.) can be seen in the RHEED image in Fig. 2.6.(d) as weak rings intersecting more intense Bragg peaks. To emphasize the diffraction ring pattern a sample rotation with fewer overlaying features has been chosen (Fig. 2.7.). For reference RHEED diffraction spots from the surface layer and the Debye-Scherrer ring pattern from the NWs have been simulated simultaneously giving a good match between diffraction spots (hollow dots) and ring positions (white half circles), as an indication of a strain free GaN crystal structure. A similar overlapping ring like pattern has been observed for slightly distorted GaN NWs grown by MBE [33].

Similar measurements have been performed on ordered GaN NW structures as seen in Figure 2.4.. The observed diffraction pattern is similar to the previous results and



2.7. Figure. RHEED image of randomly oriented GaN nanowires shows Debye-Scherrer ring patterns defined by the hexagonal lattice. White half-circles indicate calculated plane spacing. The hollow dots correspond to the simulated diffraction pattern from the GaN (0001) surface.



2.8. Figure. RHEED analysis on ordered semipolar GaN nanowires with possible $[2\overline{1}\overline{1}3]$ growth direction, where shows diffraction pattern (a) before and (b) after annealing.

depending on the sample rotation one can distinguish two high symmetry positions. The point location relative to GaN (0001) surface diffraction shows relaxed GaN wurtzite structure with c-axis oriented out of the surface (Fig. 2.8.(a)). And because NWs has an inclination to the surface, it is clear that their growth direction is different from [0001]. Taking into account that they tend to form triangular shapes (as observed in Fig. 2.5.(b) and Fig. 2.4.(b))) their most probable growth direction is along $[2\overline{1}\overline{1}3]$ as derived from TEM diffraction pattern from Figure 2.5.(a) inset. That would also explain a typical 60° threefold symmetry as observed in Figure 2.4..

The nanowires growing in a direction that is different from the high symmetry c or a axis usually have irregularly shaped [35]. Similar characteristics can be seen for our obtained nanowires. It would be also a cause to elongated RHEED diffraction spots (Fig. 2.8.(a)). Only after annealing treatment at 500 °C temperature the diffraction pattern becomes more prominent and Bragg peaks evolve into well-defined spots (Fig. 2.8.(b)). A similar procedure was repeated at the MOCVD chamber, right after GaN nanowire growth, which resulted in an increase of exciton luminescence intensity. The observed changes in NW properties indicate that a structural rearrangement is necessary, at low temperatures, for high quality GaN nanowire acquisition.

2.4. InGaN quantum dot synthesis

Immediately after the growth of the buffer layer (Section 2.1.) the process continues with InGaN quantum dot synthesis as described in section 1.1.3., where trimethylindium (TMIn) is used for indium source. Since InN is etched by hydrogen, before the process is started, the carrier gas is changed to N₂ and pressure in the camber is set to 300 mbar. In order to compensate for the rapid desorption of nitrogen from the QDs, NH₃ is set to run at the maximum possible flow, which results in III/V ratio of around 10,000. Because the aim is to obtain indium rich InGaN quantum dots, during experiments two TMIn sources are used simultaneously reaching maximum In flow of 57 µmol/min. Hereby the temperature dependence on QD structure has been studied in the range of 645 – 760 °C for different growth times. In all cases a Ga flow was set to minimum. For TMGa source, it is 20 µmol/min, but for TEGa – 10 µmol/min.

2.5. InGaN photoluminescence

To assess the indium concentration within the quantum dots structures an optically stimulated luminescence measurement were carried out after each successful MOCVD process. Using the empirical relationship between the photoluminescence peak positions, In concentration and QD band gap energy, it is possible to obtain a good idea of $In_x Ga_{1-x}N$ stoichiometric parameter x values [36–38].



2.9. Figure. InGaN quantum dot spectra at 4, 10, 11 and 12 ns at after excitation by 330 nm laser pulse. The inset shows a continuous logarithmic intensity change during the period from 0 to 100 ns.

2.5.1. Dynamics

Since InGaN QDs are located on the GaN buffer layer, all PL measurements have a strong GaN exciton luminescence, which often interferes with getting a good quality signal from InGaN quantum dot structures. But by exploiting the advantages of the experimental setup (as described in section 1.2.1.), the measurement can be shifted in time with respect to laser excitation pulse. Thus, it is possible to partially or completely get suppress the buffer contribution to PL spectra. That is possible due to the fact that GaN buffer exciton luminescence lifetime measures in picoseconds [9] while InGaN quantum dot luminescence tail exceeds 100 ns boundary (as seen from the inset of Fig. 2.9.)

An example of a typical InGaN QD PL evolution in time is shown within Figure 2.9., where the inset shows a continuous logarithmic intensity change during the period from 0 to 100 ns and colored lines denotes successive spectra at 4, 10, 11 and 12 ns at time after excitation by 330 nm laser pulse. Due to limitation of ICCD camera it is possible to resolve the time scale only with 6 ns resolution. From here one can see that at $\Delta t =$ 11 ns exciton luminescence intensity is practically extinguished, but the signal from the quantum dots decreased only to 80%. For further data acquisition a time delay of 10 ns is maintained. This allows to increase the sensitivity of ICCD camera without a fear of overexposure.



2.10. Figure. On the left side PL spectra, where black curve - experimental data ($\Delta t = 10 \text{ ns}$), dashed green curve – InGaN QD luminescence peaks and red curve – the simulated PL together with interference pattern. To the right, a schematic of Fabry-Perot interferometer analogue.

2.5.2. Interpretation

As nanoparticles are situated on the 2 µm thick GaN layer, PL spectra has a periodic minimum and maximum pattern that is attributed to interference effects coming from buffer layer (Fig. 2.10.). The effect can be described by Fabry-Perot analogue system of thin films shown on the right side of Figure 2.10.. Here a total reflected light intensity I_r is given by the equation:

$$I_r = I_0 \left(1 - \frac{1}{1 + 4F_r^2 \sin^2[2\pi n_1 L/\lambda]} \right),$$
(2.1)

where λ is a wavelength, I_0 - intensity of quantum dot luminescence, n_1 - environmental refractive index, L - layer thickness and $F_r = \sqrt{R_1 R_2}/(1-R_1 R_2)$, which depends on sapphire and GaN reflection coefficients (R_1 and R_2). In (2.1.) equation I_0 is replaced by luminescence peak profile equations.

By taking into account the n_1 dependence on the wavelength for GaN, the equation (2.1.) coincides well with the observed experimental data (Fig. 2.10. red curve). In this case it is easy to find a position of two Gaussian peaks with maximums at 2.73 eV and 2.13 eV energies (Fig. 2.10. dashed green curves). By assessing the results it can be concluded that the surface contains two different QD structures, respectfully $In_{0.2}Ga_{0.8}N$ and $In_{0.3}Ga_{0.7}N$.

2.6. InGaN quantum dot structures

Preliminary studies for the QD growth times showed a huge influence for indium concentration and the size of nanoparticles. It was observed that for the nanoparticles



2.11. Figure. The blue curve represents PL spectrum of InGaN sample with 4 min, but red - 1 min growth time. Next, the AFM $10 \times 10 \ \mu\text{m}^2$ images of the quantum structure points with the height of 50 nm and 30 nm

in the range of 30 - 40 nm indium incorporation into the crystalline lattice is stopped, reaching the point of concentration typical to thin films. If the growth time is reduced from 4 min to 1 min a huge shift in PL spectra can be observed as seen in Fig. 2.11., where the blue curve depicts PL spectra for InGaN sample with nanostructures with a height of up to 50 nm, and red - the height of 30 nm. Within AFM measurements (10×10 µm squares) it is observed that a sample with a 1 min long process has a dense population of QDs that is close to dislocation count as predicted by the SK growth process (chapter 1.1.3.). By extending the growth time particle become larger where quantum confinement effects no longer apply.

To have a better overview both samples has been investigated by SEM and RHEED. In the Fig. 2.12. top most frames are located SEM images of both samples with (a) 4 min and (b) 1 min growth times. Lower frames hold the corresponding RHEED patterns. In both cases, a bright points indicate a high concentrations of indium and dark area is GaN buffer substrate. It has to be noted here, that, in contradiction to PL results, larger particles has the highest contrast and, thus, should consist of highest indium concentration.

The answer to this question lies in the respectful RHEED images below of Fig. 2.12.. Both diffraction patterns are taken at same condition, when the incident electron beam coincides with $[1\bar{1}00]$ crystallographic direction of hexagonal structure. In this case the values of inverse lattice base vectors a^{*} and c^{*} can be measured directly from diffraction pattern. In the result, the crystallographic constant values are found to be $a = 3.54\pm0.05$ Å and $c = 5.71\pm0.1$ Å. That corresponds to a pure relaxed InN wurtzite structure. Due



2.12. Figure. At the top, SEM images of resulting quantum structures at $100k \times mag-$ nification, and, at the bottom, corresponding RHEED diffraction pattern for InGaN samples with (a) 4 min and (b) 1 min growth times.

to the fact that electron penetration depth is smaller than QD size, only the surface layers contributed to diffraction pattern. And it can be concluded that in case of high flux of TMIn, at given QD size, In is no longer incorporated into crystalline structure, but localizes on top of already formed nanoparticles.

A further reduction in time leads to smaller structures with average height under 15 nm, as determined from AFM images (Fig. 2.13.(a)). The PL spectrum of this sample was discussed already in Figure 2.10., where it was estimated that sample consists of $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ and $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ quantum dots. It is important to note that the total luminescence signal in this case is an order of magnitude more powerful than for previous samples (compare a noise level of normalized PL plots of Fig. 2.11. and Fig. 2.10.). This can be attributed to the structure and shape of InGaN nanoparticles as seen in SEM image (Fig. 2.12.). This time particles has a shape of frozen droplets with no hint of InN presence on top of them.

Since the GaN surface has a smaller volume of InGaN, in the RHEED pattern both first and zero order Laue zones are visible. Indicated by arrows with labels L₁ and L₀ in the Fig. 2.13.(c). In this case a direct comparison between GaN (0001) surface and InGaN crystallographic constants is possible. That gives a base vector values of $a = 3.51 \pm 0.07$ Å and $c = 5.35 \pm 0.1$ Å for InGaN hexagonal structure. Although by Vegard's law estimation c crystallographic constant is characterised by approximately 30% indium concentration in quantum dots, but a value approach the level of pure InN [38]. In the result RHEED patterns confirm $In_{0.3}Ga_{0.7}N$ quantum dot structure with nature of sctongly compressed hexagonal lattice.



2.13. Figure. In_{0.3}Ga_{0.7}N QD structures in (a) AFM, (b) SEM and (c) RHEED images.



2.14. Figure. Nano-SIMS obtained InGaN images of In, Ga elements and their ratio distribution on the surface of the sample with 130 nm resolution of $10\times10~\mu\text{m}^2$ unit.

2.7. InGaN structural investigations with nano-SIMS

Since most of the work the results obtained are based on indirect measurements, solutions are being sought to confirm indium containing QD composition on the surface. As a good candidate for such experiments is nano-SIMS, but, so far, the limited-resolution raised concerns as to whether this method can be applied to the small sized quantum dots.

The figure 2.14. illustrates the measurement results obtained from the sample with 1 min synthesis time (for comparison, see the Figure 2.11. inset with appropriate AFM structure). This illustrates In, Ga elements and their ratio distribution on the surface of the sample with 130 nm resolution of $10 \times 10 \text{ }\mu\text{m}^2$ unit. All images were derived

from a series of summed the signal from 200 scans. Since the average distance between particles is smaller than 130 nm, the images consist of fuzzy dots. In spite of this, one can observe a relationship between the quantum dot size and in the indium concentration. As concluded before, large QD structures get covered by InN that in nano-SIMS images are distinguished as bright spots. From here it can be concluded that the nano-SIMS is a promising tool to study the structure of InGaN QDs, where its applications will be developed in future work.

3 Conclusions

By continuing the previous work, during this thesis non-traditional solutions for RHEED analysis has been developed even further. For all cases, it is shown that *ex-situ* RHEED measurements are feasible on MOCVD grown nanowires and quantum dots giving an information about respectful crystallographic structures.

For the first time a study has been carried out on non-metallic catalyst grown GaN nanowires. Combined RHEED, SEM and TEM measurements revealed a different VLS growth characteristics, when compared to metallic catalyst assisted growth. In this case LiF keeps the interface with the surface and nanowires are pushed out of it. This results in catalyst free tips and semipolar crystalline structure with slight inclined growth $[2\bar{1}\bar{1}3]$ direction with respect to a hexagonal c axis. A following investigation on High Resolution TEM are necessary to confirm determined crystallographic structure.

For high indium concentration $In_x Ga_{1-x}N$ QD synthesis a size is essential. Above the threshold of 15 nm indium starts to form InN cap on top of quantum dots that causes photoluminescence intensity loss. RHEED studies on MOCVD grown quantum dots reveal a strongly compressed hexagonal lattice, which could be a cause for broadening of the PL band with an increase of stoichiometric ratio x.

Nano-SIMS measurements are a potent tool for direct measurements of InGaN QD composition on the surface. For best results a sample with low QD coverage is required. If a distance between particles are more than 130 nm, individual QD could be distinguished. In this case not only the overall indium concentration can be detected, but also the concentration depth profiles within the quantum dot itself.

Overall, the obtained results from the study can be used for further research and development of energy-efficient nano-LED designs.

4 Thesis

- RHEED measurements are feasible and provide a qualitative information on the crystallographic structure for outside of the chamber MOCVD grown GaN nanowires and InGaN quantum dot structures.
- On the contrary, as it would be expected with metallic catalyst assisted MOCVD grown GaN nanowires, non-metallic LiF catalyst assisted synthesized structures on GaN (0001) surface abide to nonstandard VLS growth mechanism. Growth direction is from the bottom up, where the catalyst maintains contact with the surface, resulting in a semipolar nanowire structures.
- InGaN composite materials have a fast increase in indium concentration with particle size reduction below 30 nm. Further growth above 15 nm results in a formation of a clean InN material on top of initial particles.
- MOCVD synthesized $In_xGa_{1-x}N$ structures can be investigated by high resolution scanning ion mass spectrometry (nano-SIMS), where it is possible to distinguish between Ga and In distribution on the surface, which directly provides information on the In/Ga ratio depending on the size of grown quantum dot.

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